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(19)

(54) PREPARATION OF COPOLYMERS OF ETHYLENE AND ETHYLENICALLY UNSATURATED MONOMERS, AND DISTILLATE OIL CONTAINING COPOLYMERS SO PRODUCED

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved method of preparing ethylene backbone copolymers and distillate oil compositions containing the copolymers so produced as pour depressants and flow improvers for distillate oil. The method involves free radical polymerization using an ester peroxide and the copolymers consist of 3 to 40 molar proportions of ethylene per one molar proportion of an unsaturated ester and have number average molecular weights in the range of 1,000 to 50,000.

The commercially most important ethylene-containing pour depressant and flow improvers for distillate oil are copolymers of ethylene and ethylenically unsaturated ester monomers, such as the copolymers of ethylene and vinyl alcohol esters, particularly vinyl acetate, which copolymers are well known in the prior art. For example, U.S. Patent 3,048,479 teaches copolymers of ethylene and C_3 to C_5 vinyl esters, e.g., vinyl acetate, having molecular weights of 1,000 to 3,000 according to K. Rast's method of determining mol. wt. (Ber. 55, 1051, 3727 (1922)), as pour depressants for fuels, specifically heating oils, diesel and jet fuels. The copolymers of the examples of said patent were prepared by free radical catalysis, using ditertiary butyl peroxide as the catalyst (although the patent teaches any peroxide catalyst), at temperatures of 280° to 340°F., in a solvent. U.S. Patent 3,131,168 teaches a free radical process for making ethylene-vinyl acetate copolymers as pour depressants for middle distillate using temperatures up to 440°F., a solvent such as toluene or hexane, any peroxy compound as catalyst, but preferably ditertiary butyl peroxide, and adding additional ethylene to the reaction during the polymerization. U.S. Patent 3,093,623 teaches still another method for making these ethylene-vinyl acetate pour depressants for middle distillates by continuously adding vinyl acetate and ethylene during the course of the reaction. U.S. Patent 3,250,714 teaches ethylene-vinyl acetate copolymers having molecular weights of 3500 to 7000 as V. I. improvers for lubricating oils.

More recently, British Patents 1,263,151 and 1,263,152 teach an improvement over the aforesaid U.S. patents by a polymerization temperature below about 130°C. and acyl peroxide as the initiator, as opposed to the alkyl peroxide, tert. butyl peroxide, and higher temperatures used by the aforesaid U.S. patents. By the technique of said British patents, it was found that the amount of ethylene branching was considerably reduced and copolymers produced by this method were generally superior pour point depressant and flow improvers to prior art copolymers prepared at higher temperatures with alkyl peroxides. Specifically, copolymers prepared with alkyl peroxides and high temperatures, while very effective in treating distillate fuel oil to lower the pour point, frequently result in wax crystals having large particle sizes ranging from one millimeter up to an inch in their largest dimension, depending upon the exact nature of the distillate oil, e.g., crude source, and narrowness of the boiling range. While the treated distillate oil containing these large wax crystals exhibits a pour point significantly under the original pour point of the untreated oil, in many cases, the large wax crystals will tend to plug filter equipment and lines normally used on delivery trucks and fuel oil storage systems when the oil is cooled below its cloud point, even though

above its pour point. Thus, as the oil containing the pour point depressant is cooled, the cloud point (the point at which the oil becomes cloudy due to crystallization of wax) will generally be reached at a temperature significantly above the pour point (the point at which the oil can no longer conveniently be poured). As a result, oils below their cloud point and above their pour point will be pourable, but at the same time the wax crystals that have formed, if too large, can result in plugging the aforesaid filter equipment. Copolymerizing ethylene and vinyl acetate at a low temperature with the acyl peroxides of said British Patents was able to give the good pour point reduction and in addition form smaller wax crystals during cooling of the treated oil.

The present invention represents a further improvement over the two prior art processes noted above, i.e. (1) using alkyl peroxide and high temperatures, or (2) acyl peroxides and low temperatures. The present invention therefore provides a method of preparing an ethylene copolymer by free radical initiation wherein said copolymer has a number average molecular weight by vapour phase osmometry in the range of 1,000 to 50,000 and consists of 3 to 40 molar proportions of ethylene per molar proportion of an other monomer selected from esters and mixtures of 30 to 99 mole % of said esters with 70 to 1 mole % of a C_3 to C_{16} alpha monoolefin, wherein said esters, have the general formula:

$$\begin{array}{ccc} R_1 & & H \\ | & & | \\ C & = & C \\ | & & | \\ R_2 & & R_3 \end{array}$$

wherein:

(a) R_1 is hydrogen or a methyl
(b) R_2 is $-OOCR_4$ or $-COOR_4$
(c) R_3 is hydrogen or $-COOR_4$, and
(d) R_4 is hydrogen or C_1 to C_{16} alkyl groups;

R_4 in (b) and (c) being the same or different which method comprises copolymerizing ethylene and the other monomer in an inert solvent by free radical initiation at a temperature of 150 to 350°F under an ethylene pressure of 700 to 10,000 psig using a hydrocarbon soluble initiator having a half life at 110°C of under 6 hours, and defined by the formula:

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-O-O-R'$$

where R and R′ are each alkyl groups of 2 to 20 carbon atoms each, and said initiator contains a total of 4 to 24 carbon atoms. The present invention therefore uses an ester peroxide, which in general gives a higher yield of pounds of polymer formed per pound of peroxide than either prior art processes (1) and (2) described above. This is important since the cost of initiator consumed is a relatively large expense in the commercial preparation of these polymers. In addition, the ester peroxide process of the invention can give a polymer which appears to have better solubility characteristics in oil concentrates at low temperatures than similar polymers produced with the acyl peroxide process, i.e., (2) above. This characteristic is important in handling or storage of the polymer concentrates so that separation, or sediment formation, is avoided. The effectiveness of the polymers prepared by the process of the invention in improving the flow characteristics of distillate fuel oil, appears generally superior to the polymers prepared by alkyl peroxide and about equal to those prepared with acyl peroxide.

In brief, the ester peroxides can significantly reduce the initiator cost, as compared to alkyl or acyl peroxides, in the polymerization, and can give polymers as effective in flow improvement as those prepared with acyl peroxides, but with good solubility in concentrates; and can give polymers better in flow improvement than the polymers prepared with alkyl peroxides.

The polymer produced by the method of the invention consist of 3 to 40, and preferably 3 to 20 molar proportions of ethylene per molar proportion of ethylenically unsaturated ester, which can be a single monomer or a mixture of such monomers in any proportion, said polymer being oil-soluble and having a number average molecular weight in the range of 1,000 to 50,000, preferably 1,000 to 5,000, as measured by Vapor Phase Osmometry, for example by using a Mechrolab Vapor Phase Osmometer Model 310A.

The unsaturated esters, copolymerizable with ethylene, are unsaturated mono and diesters of the general formula:

$$\begin{array}{ccc} R_1 & & H \\ | & & | \\ C & = & C \\ | & & | \\ R_2 & & R_3 \end{array}$$

wherein R_1 is hydrogen or methyl; R_2 is a $-OOCR_4$ or $-COOR_4$ group wherein R_4 is hydrogen or a C_1 to C_{16}, preferably a C_1 to C_4, straight or branched chain alkyl group; and R_3 is hydrogen or $-COOR_4$. The monomer, when R_1 and R_3 are hydrogen and R_2 is $-OOCR_4$ includes vinyl alcohol esters of C_2 to C_{17} monocarboxylic acids, preferably C_2 to C_5 monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobuyrate, vinyl laurate, vinyl myristate and vinyl palmitate. When R_2 is $-COOR_4$, such esters in-

clude methyl acrylate, methyl metacrylate, lauryl acrylate, palmityl alcohol ester of alpha-methyl-acrylic acid and C_{13} Oxo alcohol esters of methacrylic acid. Examples of monomers where R_1 is hydrogen and R_2 and R_3 are —$COOR_4$ groups, include mono and di-esters of unsaturated dicarboxylic acids such as: mono C_{13} Oxo fumarate, di-C_{13} Oxo fumarate, di-isopropyl maleate, di-lauryl fumarate and ethyl methyl fumarates.

As previously mentioned, 3 to 40 moles of ethylene will be used per mole of the unsaturated ester which is an ester as hereinbefore defined, or a mixture of 30 to 99 mole % ester and 70 to 1 mole % of a C_3 to C_{16}, preferably C_4 to C_{14}, branched or straight chain alpha monoolefin. Examples of such olefins include propylene, n-octene-1, and n-decene-1.

In general, the polymerizations can be carried out as follows: Solvent and a portion of the unsaturated ester e.g., 0—50, preferably 10 to 30 wt. %, of the total amount of unsaturated ester used in the batch, are charged to a stainless steel pressure vessel which is equipped with a stirrer. The temperature of the pressure vessel is then brought to the desired reaction temperature and pressured to the desired pressure with ethylene. Then initiator and additional amounts of the unsaturated ester are added to the vessel continuously, or at least periodically, during the reaction time, which continuous addition gives a more homogeneous copolymer product as compared to adding all the unsaturated ester at the beginning of the reaction. Also during this reaction time, as ethylene is consumed in the polymerization reaction, additional ethylene is supplied through a pressure controlling regulator so as to maintain the desired reaction pressure fairly constant at all times. Following the completion of the reaction, the liquid phase of the pressure vessel is distilled to remove the solvent and other volatile constituents of the reacted mixture, leaving the polymer as residue.

Usually, based upon 100 parts by weight of copolymer to be produced, 100 to 600 parts by weight of solvent, and 0.1 to 5, e.g., .5 to 3 parts by weight of initiator, will be used.

The solvent can be any substantially non-reactive organic solvent for furnishing a liquid phase reaction which will not poison the initiator or otherwise interfere with the reaction. Examples of solvents which may be used include C_5 to C_{10} hydrocarbons, which can be aromatic such as benzene and toluene; aliphatic such as n-heptane, n-hexane, n-octane, and isooctane; cycloaliphatic such as cyclohexane, and cyclopentane. Various polar solvents may also be used such as hydrocarbyl esters, ethers and ketones of 4 to 10 carbon atoms such as ethyl acetate, methyl butyrate, acetone, and dioxane. A particularly preferred solvent is cyclohexane which is easily handled and which gave very good utilization of the initiator.

The temperature used during the reaction will be in the range of 150 to 350°F., e.g. 200—270°F., preferably 200 to 250°F.

Free radical initiators used are those which have a half life of less than six hours at 110°C and are hydrocarbon soluble, ester peroxides of the general formula:

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}R'$$

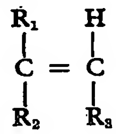
where R and R′ are each alkyl groups including alkyl, and cycloalkyl groups, either straight chain or branched chain, of 2 to 20, e.g., 4 to 12 carbon atoms each. The ester peroxide will contain a total of 4 to 24, preferably 6 to 18 carbon atoms. Some specific examples of such ester peroxides include: t-butyl peroxypivalate, t-butyl peroctoate (i.e., t-butyl peroxy-2-ethylhexanoate), t-butyl peroxyisobutyrate and t-butyl peracetate.

The pressures employed can range between 500 to 10,000 psig. However, relatively moderate pressures of 700 to 3000 psig will generally suffice with vinyl esters such as vinyl acetate. In the case of esters having a higher relative reactivity to ethylene, such as methyl methacrylate, than somewhat higher pressures, such as 3,000 to 10,000 psi have been found to give more optimum results than lower pressures. In general, the pressure should be at least sufficient to maintain a liquid phase medium under the reaction conditions, and to maintain the desired concentration of ethylene in solution in the solvent.

The time of reaction will depend upon, and is interrelated to, the temperature of the reaction, the choice of catalyst, and the pressure employed. In general, however, 1/2 to 10, usually 2 to 5 hours will complete the desired reaction.

The polymers of the invention will generally be added to distillate hydrocarbon oils in amounts of .001 to 2 wt.%, generally .005 to 0.5 wt.% said wt.% being based upon the weight of the oil to be treated.

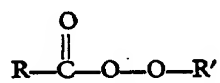
The present invention therefore also provides a distillate petroleum oil boiling in the range of 250°F to 750°F containing from .001 to 2 wt.% of a wax crystal modifier which has a number average molecular weight in the range of 1,000 to 50,000 and consists of a copolymer of 3 to 40 molar proportions of ethylene and one molar proportion of an other monomer selected from esters and mixtures of 30 to 99 mole % of said esters with 70 to 1 mole % of a C_3 to C_{16} alpha monoolefin, wherein said esters have the general formula:



wherein:

(a) R_1 is hydrogen or methyl radicals;
(b) R_2 is $—OOCR_4$ or $—COOR_4$;
(c) R_3 is hydrogen or $—COOR_4$; and
(d) R_4 is hydrogen or C_1 to C_{16} alkyl groups;

R_4 in (b) and (c) being the same or different wherein said copolymers has been prepared by copolymerizing ethylene and said other monomer in an inert solvent at a temperature of 150 to 350°F under an ethylene pressure of 700 to 10,000 psig using a hydrocarbon soluble free radical ester initiator having a half life at 110°C of under 6 hours of the formula:



wherein R and R′ are each alkyl groups of 2 to 20 carbon atoms, and said initiator contains a total of 4 to 24 carbon atoms.

The distillate hydrocarbon oils, which are treated for pour depression with the polymers of this invention, include cracked and virgin distillate oils boiling in the range of 250° to 750°F, such as heating oil and diesel fuel oil.

The polymers of the invention may be used alone as the sole oil additive, or in combination with other oil additives such as other pour depressants or dewaxing aids; corrosion inhibitors; antioxidants or sludge inhibitors.

The present invention is illustrated by the following Examples I to VII which relate to the preparation of copolymers having molecular weights and mole ratios according to the invention.

EXAMPLE I.

A stirred autoclave was charged with 4500 ml. of cyclohexane as solvent and 500 ml. of vinyl acetate. The autoclave was then purged with nitrogen and then with ethylene. The autoclave was then heated to 105°C. (about 220°F) while ethylene was pressured into the autoclave until the pressure was raised to 1050 psig. Then, while maintaining a temperature of 105°C and 1050 psig pressure, 1249 ml. of vinyl acetate was injected at a constant rate over a two hour period. At the same time, 30 grams of t-butylperoctoate diluted with 757 ml. of cyclohexane was also slowly pumped into the reactor over the two hour period at a constant rate. At the end of said two hour period, and after the last of said vinyl acetate and peroxide was injected, the batch was maintained at 105°C. for an additional 10 minutes. Then, the temperature of the reactor contents was lowered to about 60°C., the reactor was depressurized, and the contents were discharged from the autoclave. The product was then stripped of the solvent and unreacted monomers. The final stripped product consisted of about 1577 grams of copolymer of ethylene and vinyl acetate.

EXAMPLES II TO VII.

Examples II to VII were carried out following the general procedure of Example I, except that changes in pressure, temperature, or amount of peroxide were made.

COMPARISON EXAMPLES A AND B.

These comparison examples were carried out using the same general technique as in Example I, except that 54.5 grams of dilauroyl peroxide, usually designated as lauroyl peroxide (an acyl peroxide), was used in place of the 30 grams of tert. butyl peroctoate. Also, the lauroyl peroxide (as it is a solid) was added as a solution dissolved in 757 ml. of cyclohexane so it could be pumped.

Concentrates of all the above polymers were made by dissolving 45 wt. % of the polymer in 55 wt. % of a heavy aromatic naphtha (HAN) for ease in further handling.

The polymers were tested for flow improving ability at temperatures below the cloud point in a "Cold Filter Plugging Point Test" (CFPPT) which is described in detail in Journal of the Institute of Petroleum, Volume 52, Number 510, June 1966, pp. 173—185. In brief, the Cold Filter Plugging Point Test is carried out with a 45 ml. sample of the oil to be tested which is cooled in a bath maintained at about −30°F. Every two degrees drop in temperature, starting from 4°F. above the cloud point, the oil is tested with a test device consisting of a pipette to whose lower end is attached an inverted funnel. Stretched across the mouth of the funnel is a 350 mesh screen having an area of about 0.45 square inch. A vacuum of about 7″ of water is applied to the upper end of the pipette by means of a vacuum line while the screen is immersed in the oil sample. Due to the vacuum, oil is drawn across the screen up into the pipette to a mark indicating 20 ml. of oil. The test is repeated with each two degrees drop in temperature until the vacuum fails to fill the pipette to the aforesaid mark due to clogging of the screen with wax crystals. The results of the test are reported as the "operability limit" or cold filter plugging point (CFPP), which is the temperature at which the oil no longer flows.

Test Fuel A was a diesel fuel boiling in the range of about 172 to 353°C., having a cloud point of −3°C., an aniline point of 73°C., a specific gravity of 0.8193 and a viscosity of 2.64 cs. at 100°F. This fuel in the CFPPT gave a plugging point of about +28°F.

A series of blends of 0.02 wt. % of the aforesaid polymer concentrates in Fuel A were made up and then tested in duplicate using the CFPPT procedure. The following Table summarizes the preparation details of the aforesaid Examples, and Comparisons A and B, along with the yields and effectiveness in Test Fuel A.

TABLE

Polymer Preparation	I	II	III	IV	V	VI	VII	Comparison A	Comparison B
Peroxide Initiator	Peroctoate	Peroctoate	Peroctoate	Peroctoate	Peroctoate	Peroctoate	Peroctoate	Lauroyl	Lauroyl
Reaction Temp., °F.	220	250	220	250	250	235	235	220	220
Reaction Pressure, psig	1050	1050	1150	1150	1150	1150	1050	1050	1050
Initial Charges									
Cyclohexane, ml.	4500	4500	4500	4500	4500	4500	4500	4500	4500
Vinyl Acetate, ml.	500	500	500	500	500	500	500	500	500
Injection Charges over 2 Hr.									
Vinyl Acetate, ml.	1249	1249	1249	1249	1249	1249	1249	1249	1249
Initiator, (1) gm.	30	30	30	30	24	24	18	54.5	54.5
Polymer Properties									
Yield, gm.	1577	1526	1933	2296	2630	2660	2618	1987	1966
Yield (gm. Polymer/gm. Initiator)	52.6	50.9	64.4	76.5	109.6	110.8	145.4	36.5	36.1
Visc., cs. at 100°F. of 45% Polymer in HAN	130	79.4	139	—	73.2	91.6	100.5	155	128
% Vinyl Acetate (By Sap. No.)	—	—	—	—	35.9	33.9	34.8	35.9	35.1
Flow Improvement, CFPPT, °F.									
Fuel A+0.02% Concentrate	8,8	20,20	8,6	6,6	6,6	6,6	10,12	8,8	6,6

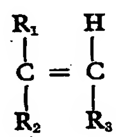
(1) Dissolved in 757 ml. of cyclohexane.

As seen from the Table, the use of the t-butyl peroctoate (i.e., t-butyl peroxy-2-ethyl-hexanoate) gave higher yields of polymer per amount of initiator than the dilauroyl peroxide. Specifically, Examples I to VII gave yields ranging from 50.9 to 145 grams of polymer per gram of initiator, as compared to the dilauroyl peroxide which in Comparisons A and B gave 36.5 and 36.1 grams of polymer per gram of initiator, respectively. Since the molecular weight of the peroctoate peroxide is about 54% that of the dilauroyl peroxide, one could have expected about an 85% increase in yield. Yet, Examples V to

VII show a much greater yield using the peroctoate than would have been expected from mere molecular weight differences. At the same time, the sets of duplicate runs in the CFPPT show that about comparable flow improvement could be obtained with the polymer prepared by the peroctoate as opposed to the dilauroyl peroxide.

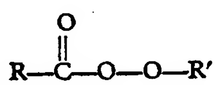
WHAT WE CLAIM IS:—

1. A method of preparing an ethylene copolymer by free radical initiation, wherein said copolymer has a number average molecular weight by vapour phase osmometry in the range of 1,000 to 50,000 and consists of 3 to 40 molar proportions of ethylene per molar proportion of an other monomer selected from esters and mixtures of 30 to 99 mole % of said esters with 70 to 1 mole % of a C_3 to C_{16} alpha monoolefin, wherein said esters, have the general formula:



wherein:
(a) R_1 is hydrogen or a methyl
(b) R_2 is —OOCR_4 or —COOR_4
(c) R_3 is hydrogen or —COOR_4, and
(d) R_4 is hydrogen or C_1 to C_{16} alkyl groups;

R_4 in (b) and (c) being the same or different which method comprises copolymerizing ethylene and the other monomer in an inert solvent by free radical initiation at a temperature of 150 to 350°F under an ethylene pressure of 700 to 10,000 psig using a hydrocarbon soluble initiator having a half life at 110°C of under 6 hours, and defined by the formula:



where R and R′ are each alkyl groups of 2 to 20 carbon atoms each, and said initiator contains a total of 4 to 24 carbon atoms.

2. A method according to claim 1 wherein said copolymer contains 3 to 20 molar proportions of ethylene, and said other monomer is an ester.

3. A method according to claim 2 wherein said ester is a vinyl alcohol ester of C_2 to C_{17} monocarboxylic acid.

4. A method according to claim 3 wherein said ester is vinyl acetate.

5. A method according to claim 3 or claim 4 wherein said copolymer has a number average molecular weight by vapour phase osmometry in the range 1000 to 5000 and the ester is a vinyl alcohol ester of a C_2 to C_5 monocarboxylic acid.

6. A method according to any one of claims 3 to 5 wherein said solvent is a C_5 to C_{10} hydrocarbon.

7. A method according to any of the preceding claims wherein said monomers are copolymerized at a temperature of 200 to 250°F and R and R′ are alkyl groups of 4 to 12 carbon atoms and said initiator contains a total of 6 to 18 carbon atoms.

8. A method according to claim 7 wherein said solvent is cyclohexane.

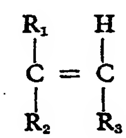
9. A method according to any of the preceding claims in which the initiator is t-butyl peroctoate.

10. A method according to claim 1 substantially as hereinbefore described with particular reference to the accompanying Examples.

11. The copolymer prepared according to the method of claims 1—10.

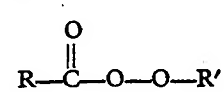
12. A copolymer of ethylene and vinyl acetate according to claim 11 having a molecular weight in the range 1,000 to 5,000.

13. A distillate petroleum oil boiling in the range of 250°F to 750°F containing from .001 to 2 wt.% of a wax crystal modifier which has a number average molecular weight in the range of 1,000 to 50,000 and consists of a copolymer of 3 to 40 molar proportions of ethylene and one molar proportion of an other monomer selected from esters and mixtures of 30 to 99 mole % of said esters with 70 to 1 mole % of a C_3 to C_{16} alpha monoolefin, wherein said esters have the general formula:



wherein:
(a) R_1 is hydrogen or methyl
(b) R_2 is —OOCR_4 or —COOR_4
(c) R_3 is hydrogen or —COOR_4; and
(d) R_4 is hydrogen or C_1 to C_{16} alkyl groups;

R_4 in (b) and (c) being the same or different wherein said copolymers has been prepared by copolymerizing ethylene and said other monomer in an inert solvent at a temperature of 150 to 350°F under an ethylene pressure of 700 to 10,000 psig using a hydrocarbon soluble free radical ester initiator having a half life at 110°C of under 6 hours of the formula:



wherein R and R′ are each alkyl groups of 2 to 20 carbon atoms, and said initiator contains a total of 4 to 24 carbon atoms.

14. A distillate oil according to claim 13 wherein said copolymer contains 3 to 20 molar proportions of ethylene and said other monomer is vinyl acetate, said temperature is 200 to 250°F, and said initiator is t-butyl peroctoate.

15. A distillate oil according to claim 13 substantially as hereinbefore described with particular reference to the accompanying examples.

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